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TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 48876

DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/646183

INTERNATIONAL APPLICATION NO. PCT/EP 99/01794

INTERNATIONAL FILING DATE 18 March 1999

PRIORITY DATE CLAIMED 20 March 1998

TITLE OF INVENTION: INHERENTLY LIGHT- AND HEAT-STABILIZED POLYAMIDES OF IMPROVED WETFASTNESS

APPLICANT(S) FOR DO/EO/US UIr/ke BREINER, Manfred JULIUS, Rainer NEUBERG, Robert WEISS, Axel WILMS, Harry Y. HU

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

- 1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
- 2. // This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
- 3. NJ This express request to begin national examination procedures (35 U.S.C.371(f)) at any time rather than delay examination unthe expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
- 4. /x/ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
- 5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b.// has been transmitted by the International Bureau.
 - c.// is not required, as the application was filed in the United States Receiving Office (RO/US0).
- 6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
- 7. /X/ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a./X/ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b.// have been transmitted by the International Bureau.
 - c.// have not been made; however, the time limit for making such amendments has NOT expired.
 - d.// have not been made and will not be made
- 8. /X/ A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).
- 9. / X/ An oath or declaration of the inventor(s)(35 U.S.C. 171(c)(4)).
- 10.// A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

- 11./X / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
- 12./ X/ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
- 13./X / A FIRST preliminary amendment
- // A SECOND or SUBSEQUENT preliminary amendment.
- 14.// A substitute specification.
- 15.// A change of power of attorney and/or address letter.
- 16./x / Other items or information. International Search Report

International Preliminary Examination Report

09/646183

U.S. Appin. No. (If Known) INTERNATIONAL APPLN. NO. PCT/EP 99/01794		EY'S DOCKET NO.
	48876	
17. /X/ The following fees are submitted BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):	CALCULATIONS	PTO USE ONLY
Search Report has been prepared by the		
EPO or JPO\$840.00	040.00	
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later than //20//30 months from the earliest		
claimed priority date (37 CFR 1.492(e)),		
claimed priority date (37 CFR 1.492(e)).		
Claims Number Filed Number Extra		
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Total Claims 13 -20	V0.40	
Indep.Claims 1 -3	X\$18.	
Multiple dependent claim(s)(if applicable) +270.	X\$78.	
TOTAL OF ABOVE CALCULATION	= 840.00	
Reduction of 1/2 for filing by small entity, if applicable.	= 840.00	
Verified Small Entity statement must also be filed		
(Note 37 CFR 1.9, 1.27, 1.28).		
	= 840.00	
Processing fee of \$130, for furnishing the English	= 840.00	
translation later than / /20 / /30 months from the		
earliest claimed priority date (37 CFR 1.492(f)). +		
TOTAL NATIONAL FEE		
Fee for recording the enclosed assignment (37 CFR 1.21(h)).	= 840.00	
The assignment must be accompanied by an appropriate cover		
sheet (37 CFR 3.28, 3.31) \$40.00 per property =	40.00	
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Registration No. 18,967

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE In re the Application of BREINER et al. BOX PCT International Application PCT/EP 99/01794 BIE BOX PCT

PRELIMINARY AMENDMENT

Honorable Commissioner of Patents and Trademarks Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

Claim 3, line 1, delete "or 2".

Claim 4, line 1, delete "any of claims 1 to 3" and insert --claim 1--.

Claim 5, line 1, delete "any of claims 1 to 4" and insert --claim 1--.

Claim 6, line 1, delete "any of claims 1 to 5" and insert --claim 1--.

Claim 7, line 1, delete "any of claims 1 to 6" and insert -- claim 1--.

Claim 8, line 1, delete "any of claims 1 to 2" and insert -- claim 1--.

Claim 9, line 1, delete "any of claims 1 to 8" and insert --claim 1--.

Claim 10, lines 1 and 2, delete "any of claims 1 to 9" and insert -claim 1--.

Claim 11, lines 1 and 2, delete "any of claims 1 to 9" and insert --claim 1--.

REMARKS

The claims were amended in the preliminary examination. The claims have been amended further to eliminate multiple dependency and to put it in btter form for U.S. filing. No new matter is included.

Favorable action is solicited.

Respectfully submitted,

KEIL & WEINKAUF

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422 Rec'd PCT/PTO 1 4 SEP 2000

Inherently light- and heat-stabilized polyamides of improved wetfastness

5 Specification

The present invention relates to a process for preparing polyamides, which comprises polymerizing starting monomers or starting oligomers in the presence of at least one compound of the formula (I)

15

$$\begin{array}{c|c}
R^2 & R^3 \\
\hline
 & N-R^1 \\
\hline
 & R^5 & R^4
\end{array}$$

20

25 where

R

is a functional group R^8 which bears 1-4 identical or different amide-forming groups \mathbf{p}^7

30 R1

35

is H, C_1-C_{20} -alkyl, cycloalkyl, benzyl or OR^6 , where

 R^6 is H, C_1 - C_{20} -alkyl, cycloalkyl or benzyl,

 R^2 , R^3 , R^4 and R^5 n

are independently C_1-C_{10} -alkyl, is a natural number greater than 1, and

the piperidine derivatives attached to R are identical or different with regard to the substituents, meaning R¹, R², R³, R⁴ and R⁵.

40 It further relates to polyamides obtainable by this process, to the use of such polyamides for preparing filaments, fibers, films, sheetlike structures and moldings, and to filaments, fibers, films, sheetlike structures and moldings comprising such a polyamide.

The preparation of polyamides, including nylon-6 and nylon-6,6, by addition or condensation polymerization from appropriate starting monomers or starting oligomers is common knowledge (Adolf Echte, Handbuch der technischen Polymerchemie, VCH 5 Weinheim, 1993, p. 553).

The application properties of such polyamides, such as heat stability, light stability, dyeability, resistance to the washing out of color (color wetfastness), are unsatisfactory for many 10 applications.

For instance, coloration problems can arise as a result of chemical changes (oxidative/thermal damage) to the polymer during carpet yarn or textile fabric heat setting. Both continuous 15 filaments and staple fibers can be affected.

It is known to add stabilizers to the polyamide to improve these properties. Such an addition can take place before, during or after the polymerization, for example during the processing.

- If the stabilizers are mixed into the polyamide and not attached to the polymer chain, they can migrate, evaporate or wash out of the polymer, so that the effectiveness of the stabilizers (air, decreases in an undesirable manner and the surroundings (air,
- 25 dyebath, cleaning baths) may become contaminated. For instance, DE-A-39 01 717 describes improving the dyeability of polyamides by adding small amounts of at least one amino or imino compound having a cycloalkyl, aryl or hetaryl moiety in the molecule.
- 30 The addition of 2,2,6,6-tetramethylpiperidine derivatives with an amide-forming group in position 4 and with or without substitution in position 1 during the polymerization is described for example in WO 95/28443, DE-A-44 13 177, WO 97/05189 and WO 97/13800. The use of these stabilizers leads to a reduction in
- 35 the rate of polymerization and hence to higher manufacturing costs for the polyamides due to a reduced space-time yield. In addition, the wetfastness of such polyamides is unsatisfactory.
- It is an object of the present invention to provide a process for 40 preparing polyamides, polyamides obtainable by this process, the use of such polyamides for preparing filaments, fibers, films, sheetlike structures and moldings, and also filaments, fibers, films, sheetlike structures and moldings comprising such a polyamide without the disadvantages mentioned.

20 US-A-3,671,542).

We have found that this object is achieved by the process for preparing polyamides defined at the beginning, polyamides obtainable by this process, the use of such polyamides for preparing filaments, fibers, films, sheetlike structures and 5 moldings, and also filaments, fibers, films, sheetlike structures and moldings comprising such a polyamide.

Polyamides are herein to be understood as being homopolymers, copolymers, blends and grafts of synthetic long-chain polyamides 10 having recurring amide groups in the polymer main chain as an essential constituent. Examples of such polyamides are nylon-6 (polycaprolactam), nylon-6,6 (polyhexamethyleneadipamide), nylon-4,6 (polytetramethyleneadipamide), nylon-6,10 (polyhexamethylene-sebacamide), nylon-7 (polyenantholactam), nylon-11 (poly-15 undecanolactam), nylon-12 (polydodecanolactam). As well as polyamides known by the generic name of nylon, polyamides further include the so-called aramids (aromatic polyamides), such as poly-meta-phenylene-isophthalamide (NOMEX® fiber, US-A-3,287,324) or poly-para-phenylene-terephthalamide (KEVLAR® fiber,

Polyamides can in principle be prepared by two methods.

In a polymerization from dicarboxylic acids and diamines and also in a polymerization from amino acids, the amino and carboxyl end groups of the starting monomers or starting oligomers react with one another to form an amide group and water. The water can subsequently be removed from the polymer. In a polymerization from carboxamides, the amino and amide end groups of the starting 30 monomers or starting oligomers react with one another to form an amide group and ammonia. The ammonia can subsequently be removed from the polymer. This form of polymerization is customarily known as a condensation polymerization or polycondensation.

35 A polymerization from lactams as starting monomers or starting oligomers is customarily known as an addition polymerization.

Suitable starting monomers or starting oligomers for preparing polyamides are for example:

monomers or oligomers of C_2 to C_{20} , preferably C_3 to C_{18} , amino acids, such as 6-aminocaproic acid, 11-aminoundecanoic acid, and also their dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of C_2 to C_{20} amino acid amides, such as 6-aminocaproamide, 11-aminoundecanoamide, and also their dimers, trimers, tetramers, pentamers or hexamers,

- ${f 5}$ monomers or oligomers of a C_2 to C_{20} , preferably C_2 to C_{12} , alkyldiamine, such as tetramethylenediamine or preferably hexamethylenediamine,
- with a C_2 to C_{20} , preferably C_2 to C_{14} , aliphatic dicarboxylic lo acid, such as sebacic acid, decanedicarboxylic acid or adipic acid.

and also dimers, trimers, tetramers, pentamers or hexamers thereof.

15

monomers or oligomers of a C_2 to C_{20} , preferably C_2 to C_{12} , alkyldiamine, such as tetramethylenediamine or preferably hexamethylenediamine,

- 20 with a C_8 to C_{20} , preferably C_8 to C_{12} , aromatic dicarboxylic acid or its derivatives, for example chlorides, such as 2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or terephthalic acid,
- 25 and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C_2 to C_{20} , preferably C_2 to C_{12} , alkyldiamine, such as tetramethylenediamine or preferably hexamethylenediamine,

30

with a C_9 to C_{20} , preferably C_9 to C_{18} , arylaliphatic dicarboxylic acid or its derivatives, for example chlorides, such as o-, m- or p-phenylenediacetic acid,

- 35 and also its dimers, trimers, tetramers, pentamers or hexamers,
 - monomers or oligomers of a C_6 to C_{20} , preferably C_6 to C_{10} , aromatic diamine, such as m- or p-phenylenediamine,
- 40 with a C₂ to C₂₀, preferably C₂ to C₁₄, aliphatic dicarboxylic acid, such as sebacic acid, decanedicarboxylic acid or adipic acid,
- and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C_6 to C_{20} , preferably C_6 to C_{10} , aromatic diamine, such as m- or p-phenylenediamine,

with a C_8 to C_{20} , preferably C_8 to C_{12} , aromatic dicarboxylic acid 5 or its derivatives, for example chlorides, such as 2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or terephthalic acid.

and also its dimers, trimers, tetramers, pentamers or hexamers, ${\bf 10}$

monomers or oligomers of a C_6 to C_{20} , preferably C_6 to C_{10} , aromatic diamine, such as m- or p-phenylenediamine,

with a C_9 to C_{20} , preferably C_9 to C_{18} , arylaliphatic dicarboxylic 15 acid or its derivatives, for example chlorides, such as o-, m- or p-phenylenediacetic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

20 monomers or oligomers of a C_7 to C_{20} , preferably C_8 to C_{18} , arylaliphatic diamine, such as m- or p-xylylenediamine,

with a C_2 to C_{20} , preferably C_2 to C_{14} , aliphatic dicarboxylic acid, such as sebacic acid, decanedicarboxylic acid or adipic 25 acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C_7 to C_{20} , preferably C_8 to C_{18} , aryl-30 aliphatic diamine, such as m- or p-xylylenediamine,

with a C_6 to C_{20} , preferably C_6 to C_{10} , aromatic dicarboxylic acid or its derivatives, for example chlorides, such as 2,6-naphthalenedicarboxylic acid, preferably isophthalic acid or 35 terephthalic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

monomers or oligomers of a C_7 to C_{20} , preferably C_8 to C_{18} , aryl-40 aliphatic diamine, such as m- or p-xylylenediamine,

with a C_9 to C_{20} , preferably C_9 to C_{18} , arylaliphatic dicarboxylic acid or its derivatives, for example chlorides, such as o-, m- or p-phenylenediacetic acid,

and also its dimers, trimers, tetramers, pentamers or hexamers,

30

monomers or oligomers of a C₂ to C₂₀, preferably C₂ to C₁₈, arylaliphatic or preferably aliphatic lactam, such as enantholactam, undecanolactam, dodecanolactam or caprolactam.

5 and also homopolymers, copolymers, blends and grafts of such starting polymers or starting oligomers.

Preference is given here to those starting monomers or starting oligomers which polymerize to form the polymides nylon-6, 10 nylon-6,6, nylon-4,6, nylon-6,10, nylon-7, nylon-11, nylon-12 and the aramids poly(meta-phenyleneisophthalamide) or poly(para-phenyleneterephthalamide), especially nylon-6 and nylon-6,6.

In the compound of the formula (I), R is a functional group 15 bearing 1-4 identical or different amide-forming groups R^7 .

R is suitably a C_1 to C_{20} , preferably C_6 to C_{18} , aromatic, preferably aliphatic unsaturated, preferably saturated, hydrocarbon R^8 bearing the 1-4 amide-forming groups R^7 .

The hydrocarbons R⁸ can bear functional groups, such as ether groups, non-amide-forming amine groups or acid groups, such as phosphonic acid, phosphoric acid, preferably sulfonic acid groups or their derivatives, preferably salts, especially alkali metal 25 salts, such as lithium, sodium or potassium salts.

In a preferred embodiment of the process of the present invention, R^8 is $C_1\text{-}C_{20}\text{-}alkylene, especially hexamethylene, having no further functional groups apart from <math display="inline">R^7.$

The amide-forming group R⁷ can be selected from -(NHR⁹), where R⁹ is H, alkyl having from 1 to 8 carbon atoms, cycloalkyl having from 3 to 10 carbon atoms or alkylene having from 2 to 20 carbon atoms, carboxyl, a carboxyl derivative group or preferably 35 -(NH)-. If R bears a plurality of groups R⁷, these groups can be

different or preferably identical.

R¹ is suitably alkyl having from 1 to 20, preferably from 1 to 18, carbon atoms, a substituted or preferably unsubstituted benzyl 40 group or a group OR6, where R6 is an alkyl group having from 1 to 20, preferably from 1 to 18 carbon atoms, a substituted or preferably unsubstituted benzyl group or preferably hydrogen. R¹ is particularly preferably hydrogen.

Suitable radicals R^2 , R^3 , R^4 and R^5 are independently alkyl having from 1 to 10 carbon atoms, preferably methyl or ethyl, especially methyl. R^2 , R^3 , R^4 and R^5 can be different or preferably identical.

The index n can be a natural number greater than 1, such as 2, 3, 4, 5 or 6, preferably 2, 3 or 4, especially 2.

The piperidine derivatives attached to R can be identical or 10 different, preferably identical.

Compound (I) can be a single chemical compound or a mixture of different compounds.

- 15 A particularly preferred compound of the formula (I) is 1,6-bis-(4-amino-2,2,6,6-tetramethylpiperidino)hexane. This compound and its preparation are common knowledge and it is commercially available for example from Aldrich Chemical Company, Inc.
- 20 The compound of the formula (I) is added to the starting monomers or to the polymerizing reaction mixture and becomes attached to the polyamide through reaction of at least one of the amideforming groups \mathbb{R}^7 . The secondary amino groups of the piperidine ring systems do not react because of steric hindrance.
- By chemically attaching the compound (I) to or within a polyamide, the process of the present invention provides polyamides having the advantageous properties mentioned at the beginning. The process of the present invention thus offers the 30 advantage of obviating the separate step otherwise necessary to improve the properties of pure polyamides by admixture of compounds. This eliminates problems or quality reductions as can arise on incorporation of such compounds following surface
- 35 incompatibility, viscosity degradation, migration, vaporization or washoff of these compounds or stresses as occur with compounding.

application to the polymer granules as a result of

- The polymerization of the starting monomers in the presence of 40 the compound (I) is preferably carried out according to customary processes. For instance, the polymerization of caprolactam in the presence of a compound (I) can be carried out for example according to the continuous or batchwise processes described in DE-A 14 95 198, DE-A 25 58 480, DE-A 44 13 177, Polymerization
- 45 Processes, Interscience, New York, 1977, p. 424-467 and Handbuch der Technischen Polymerchemie, VCH Verlagsgesellschaft, Weinheim, 1993, p. 546-554. The polymerization of 66 salt in the presence

of a compound (I) can be carried out by the customary batchwise process (see: Polymerization Processes, Interscience, New York, 1977, p. 424-467, especially 444-446) or by a continuous process, for example as described in EP-A 129 196. In principle, compound

5 (I) and the starting monomers can be introduced into the reactor separately or as a mixture. The compound (I) is preferably added according to a predetermined amount/time program.

In a preferred embodiment, the compound (I) is added to the 10 starting monomers in an amount of from 0.015 to 0.4 mol%, preferably from 0.025 to 0.25 mol%, based on 1 mol of amide groups of the polyamide. This amount is based for example on 1 mol of caprolactam when nylon-6 is to be prepared or on 0.5 mol of 66 salt when nylon-6.6 is to be prepared.

15

In a preferred embodiment of the invention, the compound (I) is combined with at least one of the customary chain regulators. Examples of suitable chain regulators are aliphatic and aromatic monocarboxylic acids such as acetic acid, propionic acid and

20 benzoic acid, aliphatic and aromatic dicarboxylic acids such as C₄-C₁₀-alkanedicarboxylic acids, preferably sebacic acid and dodecanedioic acid, especially adipic acid and azelaic acid, aliphatic C₅-C₈-cycloalkanedicarboxylic acids, especially cyclobexane-1.4-dicarboxylic acid, aromatic dicarboxylic acids

25 such as benzene- and naphthalene-dicarboxylic acids, preferably isophthalic acid, 2,6-naphthalenedicarboxylic acid, especially terephthalic acid, monofunctional amines and bifunctional amines, preferably hexamethylenediamine or cyclohexyldiamine and also mixtures of such acids and mixtures of such amines. The chain 30 regulator combination and the amounts used are selected inter

alia according to the desired polymer properties, such as viscosity or end group content. When dicarboxylic acids are used as chain regulators, it is preferable to use the chain regulator in an amount of from 0.06 to 0.6 mol%, preferably in an amount of

 $35 \ \text{from 0.1}$ to 0.5 mol%, based on 1 mol of amide group of the polyamide.

In another preferred embodiment, the polymerization of the process of the present invention is carried out in the presence 40 of at least one pigment. Preferred pigments are titanium dioxide, preferably titanium dioxide in the anatase form, or color-conferring compounds which are organic or inorganic in character. The pigments are preferably added in an amount of from 0 to 5 parts by weight, especially in an amount from 0.02 to 2 parts by 45 weight, based on 100 parts by weight of polyamide. The pigments can be added to the reactor with the starting materials or separately therefrom. The use of a compound (I) (even as a chain

regulator constituent) considerably improves the properties of the polymer compared with a polymer incorporating only pigment and no compound (I) or only pigment and one of the 2,2,6,6-tetramethylpiperidine derivatives mentioned at the

5 beginning.

The polyamides of the present invention are advantageously useful for preparing filaments, fibers, films, sheetlike structures and moldings. Filaments obtained from polyamides, especially 10 polycaprolactam, by high speed spinning at takeoff speeds of at least 4000 m/min are particularly advantageous. The filaments, fibers, films, sheetlike structures and moldings obtained using the polyamides of the present invention have many uses, for example as textile apparel or carpet fibers.

15

Examples

The relative viscosity of the polyamides was determined in 1% strength solution (1 g/100 ml) in concentrated sulfuric acid (96% 20 by weight) at 25°C.

The end group content was determined by acidimetric titration. The amino end groups were titrated with perchloro [sic] acid in a solution in 70:30 (parts by weight) phenol/methanol. The carboxyl 25 end groups were titrated with potassium hydroxide solution in a solution in benzyl alcohol.

To determine the color wetfastness, yarns were knitted up, then heat-set, dyed, treated with dye fixative and dried. The color 30 fastness was determined in accordance with ISO-E01:1994 (water fastness, severe).

The heat setting was carried out in a tenter at 196°C for 45 sec. The knit was then dyed in hot water (98°C) with a mixture of 2.53% 35 by weight of Telon Fast Red AF3G 150% (corresponding to 3.8% of Acid Red 151) and 0.50% by weight of Acid Rhodamine B 400% (corresponding to 2% of Acid Red 52) at pH 3.5. To improve the dye fixation, the knit was treated for 30 min in a solution of 2% by weight of Mesitol NBS at 77°C in water and then rinsed out with 40 water. After drying, the color fastness test was carried out. To this end, a sample of the fabric was moistened and placed between two pieces of undyed standard cloth. The three-ply stack was weighted with a standard weight and kept at 37°C for 4 h. The fastness was evaluated by comparing the depths of shade of the 45 stained adjacent fabric with a standard gray scale.

15

The UV stability of the yarns was determined in accordance with DIN 54004 (ISO 105 B 02) after 14 days' irradiation and subsequent measurement of the residual strength compared with an untreated sample.

To determine the heat-setting stability, a 5 g hank was aged for 120 sec in a thermal cabinet preheated to 185°C. Subsequently the breaking strength of the yarn was determined in comparison with an untreated yarn and reported as residual breaking strength [%].

The condensation potential was determined from the product of condensation-capable amino end groups and carboxyl end groups.

Preparation of polyamides (a)

In a 360 l vessel, a mixture of 100 kg of caprolactam, 15 kg of water and the additives of Table 1 (reported quantities in % by weight based on caprolactam) was heated to 260°C in the course of 2 hours. After decompression over 90 min, the mixture was 20 postcondensed at 260°C for 45 min.

The product was then pelletized, divided into two portions and each being extracted three times with 100 1 of water at 100°C in a 100 1 vessel for 5 hours at a time, and dried in a tumble dryer 25 at 160°C under nitrogen.

The polymers were spun on a high speed spinning machine (Ems-Inventa AG) by the H4S process at 270°C and with a winding speed of 5040 m/min to 44 dtex 12 filament yarn of round cross 30 section. The takeoff speed was 4300 m/min (duo 1), the draw ratio was 1: 1.28 (duo 2 = 5500 m/min) and the yarn tension upstream of the winder was 3 cN. The steam box was operated with 3 bar process steam, and the spin finish content of the yarn was 0.8%. The yarns had the following properties: elongation 42%, tenacity 35 5.2 cM/dtex, boiling water shrinkage 14%.

The properties of the polyamides are summarized in Table 2. The polyamides of the present invention have improved light and heat stability and also improved wetfastness over the comparative 40 polyamides.

Table 1

Additive	Terephthalic acid	4-Amino-2,2,6,6-	1,6-bis(4-Amino-2,2,6,6-
		tetramethylpiperidine	tetramethylpiperidino)hexane
Inventive Example 1	9.0	-/-	0.7
Inventive Example 2	9.0	1/1	0.5
Comparative Example 1	0.5	0.3	-/-

Table 2

Color wetfastn.	4.4	3.7	3.6
Heat-set. stab.	06	75	73
UV stab.	79	74	73
9	2945	2440	1925
CEG	74	87	- 22
AEG	71	63	41
RV	2.47	2.38	2.43
Product	Inv. 1	Inv. 2	Comp. 1

RV Relative viscosity

AEG Amino end group content in meq/kg

5 CEG Carboxyl end group content in meq/kg

KP Condensation potential

UV stab. UV stability, residual ultimate tensile

strength in %

Heat-set. stab. Heat-setting stability, residual tensile

10 strength in %

Color wetfastn. Wetfastness, AATCC gray scale

Preparation of polyamides (b)

15 The mixtures of Table 3 were sealed in a glass tube under a nitrogen atmosphere. The sealed tube was heated to 260°C for the reaction times of Table 4. The products had the RV values of Table 4.

20 Table 3

	Inv. 3	Comp. 2
	50 g of caprolactam	50 g of caprolactam
25	0.285 g of terephthalic acid	0.285 g of terephthalic acid
25	25 ml of water	25 ml of water
	0.140 g of 1,6-bis(4-amino-2,2,6,6-	0.354 g of 4-amino-2,2,6,6-
	tetramethylpiperidino)hexane	tetramethylpiperidine
	(0.2 mol% based on caprolactam)	(0.2 mol% based on caprolactam)

30 Table 4

	Reaction time	Inv. 3, RV	Inv. 3, AEG	Comp. 2, RV	Comp. 2, AEG
25	[h]				
35	0.5	1.20		1.24	
	1.5	1.78		1.81	
	3	1.98		2.01	
	6	1.99		2.08	
	9	2.1	108	2.08	70
40					

Preparation of polyamides (c)

A mixture as per Table 5 was [lacuna] to 270°C for 1 hour in a 1 liter autoclave. After decompression over 45 minutes, the 45 mixture was postcondensed at 260°C for 60 minutes. The product was

then pelletized, extracted with water and dried at $80\,^{\circ}\text{C}$. The results of Table 6 were found.

Table 5

5

	Comp. 3	Comp. 4	Inv. 4
	300 g of caprolactam	300 g of caprolactam	300 g of caprolactam
10	30 g of water	30 g of water	30 g of water
	1.68 g of terephthalic	1.68 g of terephthalic	1.68 g of terephthalic acid
10	acid	acid	
	0.84 g of	1.68 g of	2.1 g of
	4-amino-2,2,6,6-tetra-	4-amino-2,2,6,6-tetra-	1,6-bis(4-amino-2,2,6,6-
	methylpiperidine	methylpiperidine	tetramethylpiperidino)-
15	(0.2 mol% based on	(0.4 mol% based on	hexane
	caprolactam)	caprolactam)	(0.2 mol% based on
			caprolactam)

20 Table 6

Comp. 3, RV	Comp. 4, RV	Inv. 4, RV
2.40	2.32	2.47

25 Doubling the regulator content on going from Comp. 3 to Comp. 4, i.e., doubling the number of sterically hindered amino groups in the polymer, slows down the growth in molecular weight and reduces the postcondensation potential of such products. The polymer of the present invention makes it possible to introduce 30 twice the number of sterically hindered amino end groups without

reducing the postcondensation potential.

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We claim:

 A process for preparing polyamides, which comprises polymerizing starting monomers or starting oligomers in the presence of at least one compound of the formula (I)

10 $\mathbb{R} \xrightarrow{\mathbb{R}^2 \mathbb{R}^3} \mathbb{N} - \mathbb{R}^1$ 15

R

20

25

is a $C_1\!-\!C_{20}$ aliphatic saturated hydrocarbon R^8 which bears 1-4 identical or different amide-forming groups $R^7,$

R¹

is H, C_1 - C_{20} -alkyl, cycloalkyl, benzyl or OR^6 , where

R⁷

 R^6 is H, C_1-C_{20} -alkyl, cycloalkyl or benzyl, is selected from the group consisting of -(NHR⁹), carboxyl and carboxylic acid derivatives, R^9 being H, alkyl having from 1 to 8 carbon atoms, cycloalkyl having from 3 to 10 carbon atoms or alkylene having

from 2 to 20 carbon atoms, $R^2,\ R^3,\ R^4 \ and \ R^5 \quad are \ independently \ C_1-C_{10}-alkyl,$ $n \qquad \qquad is \ a \ natural \ number \ greater \ than \ 1,$

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the piperidine derivatives attached to R being identical or different with regard to the substituents, meaning R^1 , R^2 , R^3 , R^4 and R^5 ,

40

wherein the compound of the formula I is added to the starting monomers or to the polymerizing reaction mixture and becomes attached to the polymeide through reaction of at least one of the amide-forming groups R⁷.

- A process as claimed in claim 1, wherein the piperidine derivatives attached to R are identical with regard to the substituents, meaning R¹, R², R³, R⁴ and R⁵.
- 5 3. A process as claimed in claim 1 or 2, wherein R1 is H.
 - 4. A process as claimed in any of claims 1 to 3, wherein the R^2 , R^3 , R^4 and R^5 substituents on any one piperidine derivative are identical.

10

- 5. A process as claimed in any of claims 1 to 4, wherein ${\bf R}^2$ on any one piperidine derivative is methyl.
- 6. A process as claimed in any of claims 1 to 5, wherein n is 2. 15 $\,$
 - A process as claimed in any of claims 1 to 6, wherein R is a group of the formula - NH -R⁸ - NH - where R⁸ is alkylene having from 1 to 20 carbon atoms.
- 20 8. A process as claimed in any of claims 1 to 2, wherein R is $-\ NH \ -\ CH_2 \ -\ NH \ -\ .$
- A process as claimed in any of claims 1 to 8, wherein the
 polymerizing is carried out in the presence of at least one
 pigment.
 - 10. The use of a compound (I) as set forth in any of claims 1 to 9 for preparing polyamides.
- 30 11. A polyamide obtainable by a process as claimed in any of claims 1 to 9.
 - 12. The use of a polyamide as claimed in claim 11 for preparing filaments, fibers, films, sheetlike structures and moldings.
 - 13. Filaments, fibers, films, sheetlike structures and moldings comprising a polyamide as claimed in claim 11.

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Inherently light- and heat-stabilized polyamides of improved wetfastness

5 Abstract

A process for preparing polyamides comprises polymerizing starting monomers or starting oligomers in the presence of at least one compound of the formula (I)

15

10

 $\begin{array}{c|c}
R^2 & R^3 \\
\hline
 & N-R^1
\end{array}$

20

where

25

is a functional group R⁸ which bears 1-4 identical or different amide-forming groups R⁷.

R¹

is H, C_1 - C_2 0-alkyl, cycloalkyl, benzyl or OR^6 , where R^6 is H, C_1 - C_2 0-alkyl, cycloalkyl or benzyl,

 R^2 , R^3 , R^4 and R^5

are independently $C_1\text{-}C_{10}\text{-}alkyl$, is a natural number greater than 1, and

35 the piperidine derivatives attached to R are identical or different with regard to the substituents, meaning R¹, R², R³, R⁴ and R⁵.

The polyamides are useful for preparing filaments, fibers, films, 40 sheetlike structures and moldings.

Declaration, Power of Attorney

Page 1 of 4

0050/048876

We (I), the undersigned inventor(s), hereby declare(s) that:

the specification of which

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Inherently light- and heat-stabilized polyamides of improved wetfastness

W	is attached	hereto.	
[]	was filed on	1	as
	Application	n Serial No.	
	and amend	ed on	··
[x]		s PCT international application	
	Number .	PCT/EP 99/01794	
	on .	18/03/1999	
	and was an	nended under PCT Article 19	
		(SE	

We (1) hereby state that we (1) have reviewed and understand the contents of the above—identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for 'rinventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed	
19812135.0	Germany	20 March 1998	[x] Yes	[] No

Status (pending, patented,

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claim of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became a vailable between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	abandoned)
	•	

And we (1) hereby appoint Messrs, HERBERT B. KEIL, Registration Number 18,967; and RUSSEL E. WEINKAUF, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauf, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (gelephone 202–659–0100), our attorneys, with Tull power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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